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DESCRIPTION

LUBRICATING OIL ADDITIVE AND LUBRICATING OIL COMPOSITION CONTAINING
THE SAME

TECHNICAL FIELD

[0001]

The present invention relates to a lubricating oil additive and a lubricating oil composition containing the same.

BACKGROUND ART

[0002]

A metal-based cleaning agent has been conventionally added to engine oil for the purpose of lengthening the lifetime of the engine oil. The metal-based cleaning agent functions to prevent the deposition of sludge in an engine and to neutralize acid substances as by-products of the burning of fuel or as products obtained as a result of deterioration of the engine oil. Perbasic sulfonate, phenate, salicylate, or the like has been used in such metal-based cleaning agents. Of those, a metal-based cleaning agent composed of perbasic calcium sulfonate, calcium salicylate, magnesium sulfonate, or the like has been most generally used because it is relatively inexpensive and has excellent cleaning performance.

However, part of a metal-based cleaning agent is burnt together with fuel, and metal components in the metal-based cleaning agent cause various problems. To be specific, there arises the following problem: metal components released together with exhaust gas adhere

to an exhaust gas catalyst to reduce exhaust gas clarifying performance, and, in a diesel engine, reduces the particulate matter (PM) removal performance of a diesel particulate filter (DPF) and inhibits the reuse of the DPF. Therefore, a reduction in amount of a metal-based cleaning agent to be added is of great concern.

[0003]

In view of the foregoing, with a view to reducing the amount of a metal-based cleaning agent to be added, there have been proposed a lubricating oil composition blended with an ashless dispersant and a phenol-based ashless antioxidant (see, for example, Patent Document 1) and a lubricating oil composition blended with a specific amine compound (see, for example, Patent Documents 2 and 3). There has been also proposed a lubricating oil composition blended with an ashless dispersant, an oil-soluble antioxidant, and an oil-soluble dihydrocarbyl dithiophosphate and containing a small total sulfated ash content (see, for example, Patent Document 4).

[0004]

Patent Document 1: JP 2000-256690 A

Patent Document 2: JP 09-100485 A

Patent Document 3: JP 09-013067 A

Patent Document 4: JP 2877887 B

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0005]

In recent years, there has been a growing demand for a reduction in amount of metal components in lubricating oil compositions such as engine oil from the viewpoint of alleviating the load on the environment. However, it has been difficult to additionally reduce the amount of metal components in any one of the above lubricating oil compositions while maintaining cleaning performance such as sludge dispersibility or acid neutralizing property.

The present invention has been made with a view to solving such problems as described above, and an object of the present invention is to provide a lubricating oil additive which is free of metal components such as calcium or magnesium and is excellent in cleaning performance and a lubricating oil composition containing the same.

MEANS FOR SOLVING THE PROBLEMS

[0006]

The inventors of the present invention, through intensive studies on the above problems, have found that a quaternary ammonium salt having a specific base number and containing no metal components has cleaning performance comparable to or higher than that of a conventional metal-based cleaning agent, to complete the invention.

That is, the present invention relates to a lubricating oil additive containing a quaternary ammonium salt having a base number of at least 10 mgKOH/g.

Further, the present invention provides a lubricating oil

composition containing 0.1 to 10% by mass of the above lubricating oil additive based on a base oil.

The term "metal" as used in the present invention refers to a "typical metal element" and a "transition metal element".

EFFECT OF THE INVENTION

[0007]

According to the present invention, a lubricating oil additive containing a quaternary ammonium salt having a base number of at least 10 mgKOH/g can provide a lubricating oil composition having an extremely small amount of metal components such as calcium or magnesium and excellent cleaning performance.

BEST MODE FOR CARRYING OUT THE INVENTION

[0008]

The lubricating oil additive according to the present invention contains a quaternary ammonium salt having a base number of at least 10 mgKOH/g. The quaternary ammonium salt may be directly used as the lubricating oil additive, or may be mixed with base oil or any other additive to be used in a lubricating oil composition described later before being used as the lubricating oil additive.

The base number of the quaternary ammonium salt is preferably high from the viewpoint of sludge dispersibility or acid neutralizing properties. However, an excessively high base number is not preferable because such base number may increase the frictional coefficient of lubricating oil, or may deteriorate solubility into

base oil. Therefore, the base number of the quaternary ammonium salt is preferably 30 to 600 mgKOH/g, or more preferably 50 to 300 mgKOH/g.

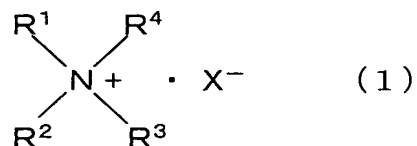
Here, the term "base number" as used in the present invention refers to the number of milligrams (mg) of potassium hydroxide in an amount equivalent to that of hydrochloric acid needed for neutralizing a basic component in 1 g of a quaternary ammonium salt. The base number can be measured by means of the total base number measuring method of JIS K2501 (petroleum product and lubricating oil-neutralization number testing method).

[0009]

Examples of such quaternary ammonium salt include quaternary ammonium salts obtained by subjecting counter anions in cationic surfactants such as tetraalkylammonium chloride and tetraalkylammonium sulfate to salt-exchange. Among them, a quaternary ammonium salt represented by the following general formula (1) is preferable.

[0010]

[Chemical formula 1]



(Where R^1 to R^4 each independently represent a hydrocarbon group having 1 to 30 carbon atoms, $-\text{R}^9\text{O}-\text{CO}-\text{R}^{10}$, or $-\text{R}^{11}\text{NH}-\text{CO}-\text{R}^{12}$ (provided

that at least one of R^1 to R^4 represents a hydrocarbon group having 1 to 30 carbon atoms), R^9 and R^{11} each represent a hydrocarbon group having 1 to 4 carbon atoms, R^{10} and R^{12} each represent a hydrocarbon group having 1 to 30 carbon atoms or a hydrogen atom, and X^- represents an anionic group.)

[0011]

Examples of a hydrocarbon group having 1 to 30 carbon atoms represented by each of R^1 to R^4 , R^{10} , and R^{12} include: alkyl groups such as a methyl group, ethyl group, propyl group, isopropyl group, butyl group, isobutyl group, secondary butyl group, tertiary butyl group, pentyl group, isopentyl group, secondary pentyl group, neopentyl group, tertiary pentyl group, hexyl group, secondary hexyl group, heptyl group, secondary heptyl group, octyl group, 2-ethylhexyl group, secondary octyl group, nonyl group, secondary nonyl group, decyl group, secondary decyl group, undecyl group, secondary undecyl group, dodecyl group, secondary dodecyl group, tridecyl group, isotridecyl group, secondary tridecyl group, tetradecyl group, secondary tetradecyl group, hexadecyl group, secondary hexadecyl group, stearyl group, eicosyl group, docosyl group, tetracosyl group, triacontyl group, 2-butyloctyl group, 2-butyldecyl group, 2-hexyloctyl group, 2-hexyldecyl group, 2-octyldecyl group, 2-hexyldodecyl group, 2-octyldodecyl group, 2-decyltetradecyl group, 2-dodecylhexadecyl group, or monomethyl-branched isostearyl group; alkenyl groups such as a vinyl

group, allyl group, propenyl group, isopropenyl group, butenyl group, isobutenyl group, pentenyl group, isopentenyl group, hexenyl group, heptenyl group, octenyl group, nonenyl group, decenyl group, undecenyl group, dodecenyl group, tetradecenyl group, or oleyl group; aryl groups such as a phenyl group, toluyl group, xylyl group, cumenyl group, mesityl group, benzyl group, phenethyl group, styryl group, cinnamyl group, benzhydryl group, trityl group, ethylphenyl group, propylphenyl group, butylphenyl group, pentylphenyl group, hexylphenyl group, heptylphenyl group, octylphenyl group, nonylphenyl group, decylphenyl group, undecylphenyl group, dodecylphenyl group, octadecylphenyl group, styrenated phenyl group, p-cumylphenyl group, phenylphenyl group, benzylphenyl group, α -naphthyl group, or β -naphthyl group; and cycloalkyl groups or cycloalkenyl groups such as a cyclopentyl group, cyclohexyl group, cycloheptyl group, methylcyclopentyl group, methylcyclohexyl group, methylcycloheptyl group, cyclopentenyl group, cyclohexenyl group, cycloheptenyl group, methylcyclopentenyl group, methylcyclohexenyl group, or methylcycloheptenyl group.

[0012]

Examples of a hydrocarbon group having 1 to 4 carbon atoms represented by each of R^9 and R^{11} includes a methyl group, ethyl group, propyl group, isopropyl group, butyl group, isobutyl group, or secondary butyl group. Of those, a linear alkyl group is preferable, and an ethyl group, propyl group, and isopropyl group

are more preferable because of easy availability of raw materials for them.

[0013]

In the above-described general formula (1), X^- represents an anionic group. X^- as an anionic group may have a value of pK_a (equilibrium constant) that is an index of acidity of more than 0 when X^- is represented as an acidic compound HX.

Examples of such anionic group include groups derived from: inorganic compounds such as carbonic acid, boric acid, and silicic acid; carbonates such as monomethyl carbonate and monoethyl carbonate; and organic carboxylic acids such as formic acid, acetic acid, propionic acid, butanoic acid (butyric acid), pentanoic acid (valeric acid), isopentanoic acid (isovaleric acid), hexanoic acid (capronic acid), heptanoic acid, isoheptanoic acid, octanoic acid (caprylic acid), 2-ethylhexanoic acid, isooctanoic acid, nonanoic acid (pelargonic acid), isononanoic acid, decanoic acid (capric acid), isodecanoic acid, undecylic acid, isoundecylic acid, dodecanoic acid (lauric acid), isododecanoic acid, tridecanoic acid, isotridecanoic acid, tetradecanoic acid (myristic acid), hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), isostearic acid, eicosanoic acid (arachic acid), docosanoic acid (behenic acid), tetracosanoic acid (lignoceric acid), hexacosanoic acid (cerotic acid), octacosanoic acid (montanic acid), 10-undecenoic acid, zoomaric acid, oleic acid, elaidic acid,

linoleic acid, linolenic acid, gadoleic acid, erucic acid, selacholeic acid, a mixed aliphatic acid obtained from natural oils and fats, malonic acid, succinic acid, maleic acid, benzoic acid, methylbenzoic acid, ethylbenzoic acid, butylbenzoic acid, hydroxybenzoic acid, naphthalenecarboxylic acid, diphenylcarboxylic acid, terephthalic acid, naphthalenedicarboxylic acid, trimellitic acid, and pyromellitic acid, and a hydroxyl group. Of those, groups derived from carbonic acid, carbonate, boric acid and an organic carboxylic acid, and a hydroxyl group are preferable because of easy availability of raw materials for them and solubility into oil.

[0014]

A quaternary ammonium salt represented by the general formula (1) of the present invention can be manufactured as follows. At least one tertiary amine selected from the group consisting of tertiary amine compounds, tertiary amineamide compounds, tertiary amine ester compounds, and tertiary amineamide ester compounds is used as a starting material. Then, the tertiary amine is quaternized with a quaternizing agent. It should be noted that well-known methods may be used for salt-exchange when a counter anion of the compound obtained by quaternization is a group other than the above-described anionic groups. In addition, when an anionic group of the quaternary ammonium salt obtained by quaternization or salt-exchange is a hydroxyl group, the hydroxyl group is neutralized with the

above-described acidic compound HX and produced water is dehydrated. As a result, the hydroxyl group can be replaced with an anionic group derived from an organic carboxylic acid.

[0015]

Examples of a tertiary amine compound which is a starting material include: alkyl tertiary amines such as trimethylamine, triethylamine, tripropylamine, tributylamine, triamylamine, trihexylamine, triheptylamine, trioctylamine, trinonylamine, tridecylamine, tridodecylamine, tritetradecylamine, trihexadecylamine, trioctadecylamine, trieicosylamine, tridocosylamine, tritetracosylamine, trihexacosylamine, trioctacosylamine, triacontylamine, monomethyldiethylamine, monomethyldibutylamine, monomethyldihexylamine, monomethyldioctylamine, monomethyldidecylamine, monomethyldidodecylamine, monomethylditetradecylamine, monomethyldihexadecylamine, monomethyldioctadecylamine, monomethyldieicosylamine, monomethyldidocosylamine, monomethylditetracosylamine, monomethyldihexacosylamine, monomethyldioctacosylamine, monomethyldiacontylamine, dimethylmonoethylamine, dimethylmonoethylamine, dimethylmonopropylamine, dimethylmonobutylamine, dimethylmonoamylamine, dimethylmonohexylamine, dimethylmonoheptylamine, dimethylmonooctylamine, dimethylmonononylamine, dimethylmonodecylamine,

dimethylmonododecylamine, dimethylmonotetradecylamine,
 dimethylmonoheptadecylamine, dimethylmonooctadecylamine,
 dimethylmonoeicosylamine, dimethylmonodocosylamine,
 dimethylmonotetracosylamine, dimethylmonoheptacosylamine,
 dimethylmonooctacosylamine, and dimethylmonoacetylamine;
 tertiary amines each having an alkenyl group such as triallylamine,
 tripropenylamine, triisopropenylamine, tributenylamine,
 triisobutenylamine, tripentenylamine, triisopentenylamine,
 trihexenylamine, triheptenylamine, trioctenylamine,
 trinonenylamine, tridecenylamine, tridodecenylamine,
 tritetradecenylamine, trioleyenylamine, monomethyldiallylamine,
 monomethyldipropenylamine, monomethyldiisopropenylamine,
 monomethyldibutenylamine, monomethyldiisobutenylamine,
 monomethyldipentenylamine, monomethyldiisopentenylamine,
 monomethyldihexenylamine, monomethyldiheptenylamine,
 monomethyldioctenylamine, monomethyldinonenylamine,
 monomethyldidecenylamine, monomethyldidodecenylamine,
 monomethylditetradecenylamine, monomethyldioleyenylamine,
 dimethylmonoallylamine, dimethylmonopropenylamine,
 dimethylmonoisopropenylamine, dimethylmonobutenylamine,
 dimethylmonoisobutenylamine, dimethylmonopentenylamine,
 dimethylmonoisopentenylamine, dimethylmonoheptenylamine,
 dimethylmonoheptenylamine, dimethylmonooctenylamine,
 dimethylmonononenylamine, dimethylmonodecenylamine,

dimethylmonododecenylamine, dimethylmonotetradecenylamine, and
 dimethylmonooleylamine; tertiary amines each having an aryl group
 such as triphenylamine, tritoluylamine, trixylylamine,
 tricumenylamine, tribenzylamine, tristyrylamine, tricinnamylamine,
 tribenzhydrylamine, triethylphenylamine, tripropylphenylamine,
 tributylphenylamine, trihexylphenylamine, trioctylphenylamine,
 trinonylphenylamine, tridecylphenylamine, tridodecylphenylamine,
 tristyrenated phenylamine, tri-p-cumylphenylamine,
 tribenzylphenylamine, tri- α -naphthylamine, tri- β -naphthylamine,
 monomethyldiphenylamine, monomethylditoluylamine,
 monomethyldixylylamine, monomethyldicumenylamine,
 monomethyldibenzylamine, monomethyldistyrylamine,
 monomethyldicinnamylamine, monomethyldibenzhydrylamine,
 monomethyldiethylphenylamine, monomethyldipropylphenylamine,
 monomethyldibutylphenylamine, monomethyldihexylphenylamine,
 monomethyldioctylphenylamine, monomethyldinonylphenylamine,
 monomethyldidecylphenylamine, monomethyldidodecylphenylamine,
 monomethyldistyrenated phenylamine,
 monomethyldi-p-cumylphenylamine, monomethyldibenzylphenylamine,
 monomethyldi- α -naphthylamine, monomethyldi- β -naphthylamine,
 dimethylmonophenylamine, dimethylmonotoluylamine,
 dimethylmonoxylylamine, dimethylmonocumenylamine,
 dimethylmonobenzylamine, dimethylmonostyrylamine,
 dimethylmonocinnamylamine, dimethylmonobenzhydrylamine,

dimethylmonoethylphenylamine, dimethylmonopropylphenylamine,
 dimethylmonobutylphenylamine, dimethylmonoethylphenylamine,
 dimethylmonooctylphenylamine, dimethylmonononylphenylamine,
 dimethylmonodecylphenylamine, dimethylmonododecylphenylamine,
 dimethylmonostyrenated phenylamine,
 dimethylmono-p-cumylphenylamine, dimethylmonobenzylphenylamine,
 dimethylmono- α -naphthylamine, and dimethylmono- β -naphthylamine;
 and tertiary amines derived from a raw material aliphatic acid
 obtained from natural oils and fats such as vegetable oils, for
 example, a linseed oil, olive oil, cacao oil, sesame oil, rice bran
 oil, safflower oil, soybean oil, camellia oil, corn oil, rapeseed
 oil, palm oil, palm kernel oil, castor oil, sunflower oil, cotton
 oil, and coconut oil and animal oils and fats, for example, beef
 tallow, lard, milk fat, fish oil, and whale oil.

[0016]

A tertiary amineamide compound which is a starting material
 can be manufactured by the following method. An amine compound such
 as: triamine having two primary amine groups and one secondary amine
 group such as diethylenetriamine, dipropylenetriamine, or
 ethylenepropylenetriamine; a triamine having two primary amine
 groups and one tertiary amine group such as
 bis(3-aminopropyl)methylamine, bis(3-aminopropyl)ethylamine,
 bis(3-aminopropyl)propylamine, bis(3-aminopropyl)butylamine, or
 bis(3-aminopropyl)benzylamine; or a diamine having one primary amine

group such as N,N-dimethylethylenediamine, N,N-diethylethylenediamine, N,N-dipropylethylenediamine, N,N-dibutylethylenediamine, N,N-dimethylpropylenediamine, N,N-diethylpropylenediamine, N,N-dipropylpropylenediamine, or N,N-dibutylpropylenediamine is allowed to react with aliphatic acid, aliphatic acid chloride, or aliphatic acid ester to amidate a primary amine group of the amine compound. As a result, an amineamide compound is obtained. When the obtained compound is a secondary amineamide compound, the secondary amine group can be tertiarized with halogenated hydrocarbon, dialkylsulfate, or the like to thereby obtain a tertiary amineamide compound.

[0017]

Examples of a tertiary amine ester compound which is a starting material include tertiary alkanolamines such as triethanolamine, N-methyldiethanolamine, N-ethyldiethanolamine, N-propyldiethanolamine, N-isopropyldiethanolamine, N-butyldiethanolamine, N,N-dimethylethanolamine, N,N-diethylethanolamine, N,N-dipropylethanolamine, N,N-dibutylethanolamine, N-cyclohexyldiethanolamine, N-benzoyldiethanolamine, tripropanolamine, triisopropanolamine, N-cyclohexyldiisopropanolamine, N-benzoyldiisopropanolamine, and tributanolamine.

In addition, the tertiary amine ester compound can also be obtained as follows. A primary alkanolamine or secondary

alkanolamine such as monoethanolamine, diethanolamine, N-methylethanolamine, N-ethylethanolamine, N-propylethanolamine, N-isopropylethanolamine, N-butylethanolamine, N-cyclohexylethanolamine, N-benzylethanolamine, monopropanolamine, dipropanolamine, monoisopropanolamine, diisopropanolamine, N-cyclohexylisopropanolamine, N-benzylisopropanolamine, monobutanolamine, or dibutanolamine is tertiarized with halogenated hydrocarbon, dialkylsulfate, or the like. After that, the resultant is allowed to react with aliphatic acid, aliphatic acid chloride, or aliphatic acid ester to esterify a hydroxyl group of the amine compound.

[0018]

A tertiary amineamide ester compound which is a starting material can be manufactured by the following method. An alcanoldiamine such as N-methanolethylenediamine, N-ethanolethylenediamine, N-propanolethylenediamine, N-butanolethylenediamine, N,N-dimethanolethylenediamine, N,N-diethanolethylenediamine, N,N-dipropanolethylenediamine, N,N-dibutanolethylenediamine, N-methanolpropylenediamine, N-ethanolpropylenediamine, N-propanolpropylenediamine, N-butanolpropylenediamine, N,N-dimethanolpropylenediamine, N,N-diethanolpropylenediamine, N,N-dipropanolpropylenediamine, or N,N-dibutanolpropylenediamine is allowed to react with aliphatic acid, aliphatic acid chloride, or aliphatic acid ester. Then, a

primary amine group and a hydroxyl group of the alcanoldiamine are subjected to an amidation reaction and an esterification reaction. As a result, an amineamide ester compound can be obtained. When the obtained compound is a secondary amineamide ester compound, the secondary amine group can be tertiarized with halogenated hydrocarbon, dialkylsulfate, or the like to thereby obtain a tertiary amineamide ester compound.

[0019]

Examples of an aliphatic acid to be used in the amidation of a primary amine group or in the amidation and esterification of a primary amine group and a hydroxyl group include formic acid, acetic acid, propionic acid, butanoic acid (butyric acid), pentanoic acid (valeric acid), isopentanoic acid (isovaleric acid), hexanoic acid (capronic acid), heptanoic acid, isoheptanoic acid, octanoic acid (caprylic acid), 2-ethylhexanoic acid, isooctanoic acid, nonanoic acid (pelargonic acid), isononanoic acid, decanoic acid (capric acid), isodecanoic acid, undecanoic acid, isoundecanoic acid, dodecanoic acid (lauric acid), isododecanoic acid, tridecanoic acid, isotridecanoic acid, tetradecanoic acid (myristic acid), hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), isostearic acid, eicosanoic acid (arachic acid), docosanoic acid (behenic acid), tetracosanoic acid (lignoceric acid), hexacosanoic acid (cerotic acid), octacosanoic acid (montanic acid), 10-undecenoic acid, zoomaric acid, oleic acid, elaidic acid,

linoleic acid, linolenic acid, gadoleic acid, erucic acid, and selacholeic acid. Mixed aliphatic acids produced from natural fats and oils are also available. Examples of the natural fats and oils include: vegetable fats and oils such as linseed oil, perilla oil, oiticica oil, olive oil, cacao oil, kapok oil, white mustard oil, sesame oil, rice bran oil, safflower oil, shea nut oil, china wood oil, soybean oil, tea oil, camellia oil, corn oil, rapeseed oil, palm oil, palm kernel oil, castor oil, sunflower oil, cottonseed oil, coconut oil, haze wax, and peanut oil; and animal fats and oils such as horse tallow, beef tallow, hoof oil, ghee, lard, goat tallow, mutton tallow, milk fat, fish oil, and whale oil.

[0020]

A known method can be used as a reaction method for quaternarization. Generally, the method involves: loading tertiary amine into an autoclave; adding a quaternarizing agent at 60°C to 200°C; and aging the resultant till the completion of a reaction. Pressurization may be performed in an inert gas such as nitrogen or helium with a view to increasing a reaction velocity or a reaction rate. The amount of the quaternarizing agent to be added is 1.0 to 4.0 mol, preferably 1.1 to 2.5 mol, or more preferably 1.1 to 1.8 mol with respect to 1 mol of the tertiary amine. An excessively small amount of the quaternarizing agent to be added may fail to complete the reaction. An excessively large amount of the quaternarizing agent to be added may cause a large amount of an

unreacted quaternarizing agent to remain to have an adverse effect on an environment such as the release of the agent to the atmosphere.

[0021]

Examples of a quaternarizing agent to be used for quaternarization include: organic halides such as methyl chloride, benzyl chloride, cyclohexyl chloride, methyl bromide, benzyl bromide, and cyclohexyl bromide; dialkyl sulfates such as dimethyl sulfate and diethyl sulfate; dialkyl carbonates such as dimethyl carbonate and diethyl carbonate; and trialkyl phosphates such as trimethyl phosphate and triethyl phosphate. Of those, methyl chloride and dimethyl carbonate are preferably used because of easy availability of raw materials for them and their ease of handling.

[0022]

Known methods can be used as a method for salt-exchange without any limitation. Examples of such a method include: a method involving synthesizing quaternary ammonium hydroxide from a quaternary ammonium halide salt, which is obtained by reacting a tertiary amine and an alkyl halide, by means of an electrolytic method (JP 45-28564 B), an ion-exchange resin method (JP 52-3009 A), or the like, neutralizing the quaternary ammonium hydroxide with an acid compound HX, and removing produced water; and a method involving reacting a quaternary ammonium halide salt and an inorganic alkali such as sodium hydroxide or potassium hydroxide, removing the produced inorganic salt to provide quaternary ammonium hydroxide, and

neutralizing the quaternary ammonium hydroxide with an acid compound HX.

[0023]

Meanwhile, an organic solvent can be used in a quaternarization reaction and a salt-exchange reaction as long as the solvent does not inhibit any one of the reactions. The organic solvent that can be used in the reactions is not particularly limited. Specific examples of such solvent include: aliphatic, alicyclic, aromatic, and heterocyclic compounds, or a mixture of them; and general lubricating oil. More specific examples of such solvent include: alkanes such as pentane, hexane, heptane, cyclopentane, cyclohexane, ligroin, and petroleum ether; alcohols such as methanol, ethanol, propanol, 2-propanol, butanol, 2-butanol, pentanol, hexanol, heptanol, octanol, and 2-ethylhexanol; alkyl ethers such as dimethyl ether, ethylmethyl ether, diethyl ether, methyl isobutyl ether, and ethyl isopropyl ether; ketones such as acetone, ethyl methyl ketone, and methyl isobutyl ketone; aromatic compounds such as benzene, toluene, xylene, and ethylbenzene; synthetic oils such as poly- α -olefin, an ethylene- α -olefin copolymer, polybutene, an alkylbenzene, an alkyl naphthalene, polyalkylene glycol, polyphenyl ether, an alkyl-substituted diphenyl ether, a polyol ester, a dibasic ester, silicone oil, and fluorinated oil; and paraffin-based mineral oil and naphthene-based mineral oil, or purified mineral oils obtained by purifying them. Of those, alkanes (such as hexane,

heptane, and petroleum ether), alcohols (such as methanol, ethanol, propanol, and 2-propanol), aromatic compounds (such as benzene, toluene, and xylene), paraffin-based mineral oil, naphthene-based mineral oil, and the like are preferable from the viewpoints of the solubility and handleability of a reaction product. In addition, adding any one of those solvents is preferable for effectively removing by-products and impurities and for dissolving solid reaction products.

[0024]

The lubricating oil composition according to the present invention contains 0.1 to 10%, or preferably 0.2 to 8% by mass of the above lubricating oil additive based on a base oil. Within the content range, cleaning performance such as sludge dispersibility or acid neutralizing property can be improved without any impairment of lubricity.

The base oil has only to be a base oil generally used in lubricating oil. Specific examples of the base oil include mineral oil, hydrocarbon-based synthetic oil, and a mixture of them. More specific examples of the base oil include: synthetic oils such as poly- α -olefin, ethylene- α -olefin copolymers, polybutene, alkylbenzene, alkyl naphthalene, polyalkylene glycol, polyphenyl ether, an alkyl-substituted diphenyl ether, polyol ester, dibasic ester, phosphate, phosphite, carbonate, silicone oil, and fluorinated oil; and paraffin-based mineral oil and naphthene-based

mineral oil, or purified mineral oils obtained by purifying them.

[0025]

The lubricating oil composition of the present invention does not inhibit the addition of any known lubricating oil additive. The composition may be added with, for example, antioxidants, organic molybdenum-based additives, extreme pressure agents, oiliness improvers, metal-based cleaning agents, dispersants, viscosity index improvers, pour depressants, rust inhibitors, corrosion inhibitors, or defoaming agents for an intended purpose.

[0026]

Examples of the antioxidant include a zinc dithiophosphate-based antioxidant, a phenol-based antioxidant, and an amine-based antioxidant. The preferable loading of any one of those antioxidants is 0.1 to 5% by mass based on the base oil.

[0027]

Examples of the organic molybdenum-based additive include: oxymolybdenum dithiocarbamate sulfide; oxymolybdenum dithiophosphate sulfide; aliphatic molybdenum salts; oxymolybdenum xanthate sulfide; reaction products between molybdenum trioxide and acid phosphate; reaction products between molybdenum trioxide and aliphatic diethanol amide; reaction products between molybdenum trioxide and glycerin monoaliphatic acid ester; reaction products between succinimide, amide carboxylate, Mannich base, or a boride of any one of them and molybdenum trioxide; and reaction products

between amine and a molybdenum compound having a pentavalent or hexavalent molybdenum atom. The preferable loading of any one of those organic molybdenum-based additives is 0.001 to 5% by mass based on the base oil.

[0028]

Examples of the extreme pressure agent include: sulfur-based compounds such as sulfurized fats and oils, olefin polysulfide, and dibenzyl sulfide; phosphor compounds such as mono-octyl phosphate, tributyl phosphate, triphenyl phosphite, tributyl phosphite, and thiophosphate; and organometallic compounds such as metal thiophosphates, metal thiocarbamates, and acid metal phosphates. The preferable loading of any one of those extreme pressure agents is 0.1 to 10% by mass based on the base oil.

[0029]

Examples of the oiliness improver include: higher alcohols such as oleyl alcohol and stearyl alcohol; aliphatic acids such as oleic acid and stearic acid; esters such as oleyl glycerin ester, lauryl glycerin ester, oleyl sorbitan ester, and oleyl trimethylolpropane ester; amides such as laurylamide, oleylamide, and stearylamine; amines such as laurylamine, oleylamine, and stearylamine; and ethers such as lauryl glycerin ether and oleyl glycerin ether. The preferable loading of any one of those oiliness improvers is 0.1 to 10% by mass based on the base oil.

[0030]

Examples of the metal-based cleaning agent include the sulfonates, phenates, salicylates, phosphonates, and perbasic salts of calcium, magnesium, barium, and the like. The loading of any one of those metal-based cleaning agents is preferably small from the viewpoint of the alleviation of the load on the environment. When the lubricating oil composition needs to have additional cleaning properties, the composition may be blended with 0 to 10%, or preferably 0 to 5% by mass of any one of those metal-based cleaning agents based on the base oil.

[0031]

Examples of the dispersant include succinimide, benzylamine, succinate, and boron-denatured products of them. The preferable loading of any one of those dispersants is 0.5 to 10% by mass based on the base oil.

[0032]

Examples of the viscosity index improver include: polyalkyl methacrylate (having 1 to 18 carbon atoms), alkyl acrylate (having 1 to 18 carbon atoms)/alkyl methacrylate (having 1 to 18 carbon atoms) copolymers; diethylaminoethyl methacrylate/alkyl methacrylate (having 1 to 18 carbon atoms) copolymers; ethylene/alkyl methacrylate (having 1 to 18 carbon atoms) copolymers; polyisobutylene; polyalkylstyrene; ethylene/propylene copolymers; styrene/maleate copolymers; styrene/maleic acid amide copolymers; styrene/butadiene hydrogenated copolymers; and

styrene/isoprene hydrogenated copolymers. Each of those viscosity index improvers has an average molecular weight of about 10,000 to 1,500,000. The preferable loading of any one of those viscosity index improvers is 0.1 to 20% by mass based on the base oil.

[0033]

Examples of the pour depressant include polyalkylmethacrylate, polyalkyl acrylate, polyalkylstyrene, and polyvinyl acetate. Each of those pour depressants has an average molecular weight of about 1,000 to 100,000. The preferable loading of any one of those pour depressants is 0.005 to 3% by mass based on the base oil.

[0034]

Examples of the rust inhibitor include: sodium nitrite; oxidized paraffin wax calcium salts; oxidized paraffin wax magnesium salts; beef tallow aliphatic acid alkali metal salts, alkali earth metal salts, or amine salts; alkenyl succinic acid or alkenyl succinic acid half esters (in which an alkenyl group has a molecular weight of about 100 to 300); sorbitan monoesters; pentaerythritol monoesters; nonylphenol ethoxylates; lanolin aliphatic acid esters; and lanolin aliphatic acid calcium salts. The preferable loading of any one of those rust inhibitors is 0.01 to 5% by mass based on the base oil.

[0035]

Examples of the corrosion inhibitor include benzotriazole, benzoimidazole, benzothiazole, and tetraalkylthiuram disulfide.

The preferable loading of any one of those corrosion inhibitors is 0.01 to 3% by mass based on the base oil.

[0036]

Examples of the defoaming agent include polydimethyl silicone, trifluoropropylmethyl silicone, colloidal silica, polyalkyl acrylate, polyalkyl methacrylate, alcohol ethoxy/propoxylate, aliphatic acid ethoxy/propoxylate, and sorbitan partial aliphatic acid ester. The preferable loading of any one of those defoaming agents is 0.001 to 1% by mass based on the base oil.

[0037]

The lubricating oil composition of the present invention can be suitably used in any one of automobile and industrial greases typified by internal combustion engine lubricating oil, driving system lubricating oil (such as manual transmission oil, differential gear oil, or automatic transmission oil), lubricating oil for metal working, and grease for constant velocity joints. Of those, the composition can be suitably used in lubricating oil for internal combustion engines such as gasoline engines, diesel engines, or jet engines.

EXAMPLES

[0038]

Hereinafter, the present invention will be described more specifically by way of examples. In the following examples, the term "%" means "% by mass" unless otherwise stated.

At first, a reference oil having the formulation shown below was prepared. Next, a lubrication oil composition of each of Examples 1 to 5 and Comparative Examples 1 to 5 was prepared by means of the following reference oil and each additive according to the formulation shown in Table 1 below. In each of Examples 1 to 5 and Comparative Examples 1 to 4, an additive was added in such a manner that the total base number of a lubricating oil composition would be 5 mgKOH/g.

<Base oil>

Mineral oil-based high-viscosity-index (VI) oil

Dynamic viscosity 4.1 mm²/s (at 100°C), 18.3 mm²/s (at 40°C),
viscosity index (VI) = 126

[Reference oil formulation]

Base oil	100 parts by mass
Succinimide-based dispersant	5.0 parts by mass
Phenol-based antioxidant	0.3 part by mass
Amine-based antioxidant	0.3 part by mass
Zinc dithiophosphate	1.0 part by mass

[0039]

<Additive>

(A-1: product of the present invention)

Dioleyl dimethyl ammonium bicarbonate

Base number: 92 mgKOH/g

Metal component: 0%

(A-2: product of the present invention)

Dioleyl dimethyl ammonium propionate

Base number: 90 mgKOH/g

Metal component: 0%

(A-3: product of the present invention)

Tridecyl monomethyl ammonium bicarbonate

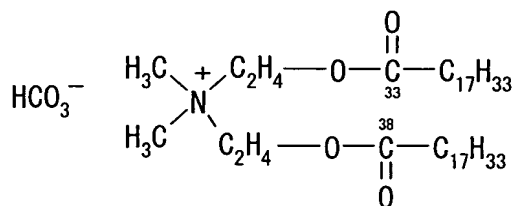
Base number: 93 mgKOH/g

Metal component: 0%

(A-4: product of the present invention)

[0040]

[Chemical formula 2]



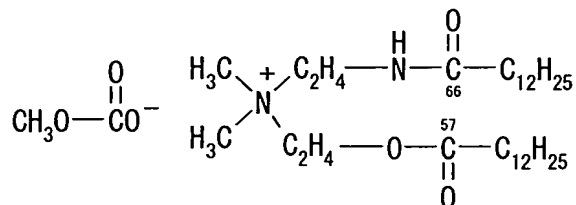
Base number: 77 mgKOH/g

Metal component: 0%

(A-5: product of the present invention)

[0041]

[Chemical formula 3]



Base number: 95 mgKOH/g

Metal component: 0%

(B-1: product of comparative example)

Calcium sulfonate

Base number: 300 mgKOH/g

Metal component: 12.6%

(B-2: product of comparative example)

Calcium sulfonate

Base number: 100 mgKOH/g

Metal component: 4.3%

(B-3: product of comparative example)

Magnesium salicylate

Base number: 200 mgKOH/g

Metal component: 3.1%

(B-4: product of comparative example)

Dioleoyl dimonomethyl amine

Base number: 105 mgKOH/g

Metal component: 0%

(B-5: product of comparative example)

Dioleoyl dimethyl ammonium chloride

Base number: 0 mgKOH/g

Metal component: 0%

[0042]

<Test of sample oil for oxidation stability>

In conformance with JIS K-2514 (lubricating oil-oxidation stability testing method), 250 ml of a sample were placed into a

glass vessel having incorporated therein a copper plate and an iron plate as catalysts, and the whole was heated at 165.5°C for one week while the sample was stirred at 1,300 rpm in such a manner that air would be involved. The dynamic viscosity (40°C) and total base number of a lubricating oil composition were measured before and after the test. A difference in dynamic viscosity was determined from the dynamic viscosity before the test and the dynamic viscosity after the test. The amount of a reduction in total base number was determined from the total base number before the test and the total base number after the test. The lubricating oil composition after the test was filtered, washed with toluene, and dried. Then, the amount of produced sludge was measured.

Oxidation stability is higher as a difference between the dynamic viscosity before the test and the dynamic viscosity after the test is smaller and the amount of a reduction in total base number is smaller. The corrosion of a metal is reduced and dispersibility is higher as the amount of produced sludge is smaller. Table 1 shows the results.

[0043]

[Table 1]

	Additive (%)	Dynamic viscosity (mm ² /S, 40°C)		Total base number (mgKOH/g)		Sludge amount (g)	Metal component (ppm)
		Before	After	Difference	Before	After	
Reference oil	-	60.5	55.8	4.7	0.96	<0	0
Example	1	67.5	66.6	0.9	5.08	3.11	0
	2	68.3	67.7	0.6	5.02	3.01	0
	3	67.8	67.4	0.4	5.03	3.02	0
	4	67.2	66.8	0.4	5.06	3.01	0
	5	67.7	67.1	0.6	5.01	3.10	0
Comparative Example	1	69.5	69.0	0.5	5.05	3.04	1,640
	2	70.8	70.0	0.8	5.03	3.00	1,720
	3	70.1	69.5	0.6	5.06	2.98	620
	4	65.3	61.3	4.0	5.12	<0	0
	5	66.0	58.2	7.8	0.97	<0	0

* The term "additive (%)" represents an addition ratio of an additive to the reference oil.

* A metal component shown is derived from a cleaning agent.

* The difference in total base number of each of the reference oil and B-5 is not written because the total base number of each of them before the test is about 1 and the total base number of each of them after the test is equal to or less than 0.

[0044]

As is apparent from Table 1, the lubricating oil composition of the present invention had a difference in dynamic viscosity of 0.4 to 0.9 mm²/S and an amount of a reduction in total base number of 1.91 to 2.05 mgKOH/g. That is, the composition showed excellent oxidation stability. In addition, the composition had a sludge amount of 0.0338 to 0.0421 g. That is, the composition showed excellent sludge dispersibility. In addition, the composition was comparable to or better than any one of the lubricating oil compositions with the conventional metal-based cleaning agents added (B-1 to B-3) in terms of all of a difference in dynamic viscosity, a sludge amount, and the amount of a reduction in total base number. Furthermore, the lubricating oil composition of the present invention does not reduce the exhaust gas clarifying performance of an exhaust gas catalyst or the particulate matter removing performance of a diesel particulate filter even when the composition is used in internal combustion engine lubricating oil because the

composition does not contain any metal components derived from a cleaning agent.

In contrast, each of the lubricating oil compositions of Comparative Example 4 added with the tertiary amine compound (B-4) having a base number of 105 mgKOH/g and the lubricating oil composition of Comparative Example 5 added with the quaternary ammonium salt (B-5) having a base number of 0 mgKOH/g was poor in oxidation stability and sludge dispersibility.